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Modeling Growth of Au-Cu Nanocrystalline Coatings

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The electrodeposition process parameters of current density, pulse duration, and cell potential affect both the structure and composition of the foils. The mechanism for nucleation and growth as determined from current transients yield relationships for nucleus density and nucleation rate. To develop an understanding of the role of the process parameters on grain size – as a design structural parameter to control strength, for example, a formulation is presented to model the affects of the deposition energetics on grain size and morphology. An activation energy for the deposition process is modeled that reveals different growth mechanisms, wherein nucleation and diffusion effects are each dominant as dependent upon pulse duration. A diffusion coefficient common for each of the pulsed growth modes demarcates an observed transition in growth from smooth to rough surfaces.

Coatings of gold-copper (Au-Cu) are prepared through the aqueous process of pulsed plating metals from an ionic solution. The current (i) and cell potential (U) are measured between an inert platinum anode and a cathode (sheet of titanium). A basic No. 2 Au bath is used as heated to a temperature of 55-75 °C with a pH of ~11. The surfaces of 10-30 μm thick foils are imaged using a scanning electron microscope. Also, the film composition is measured using energy dispersive x-ray spectra. Morphologies seen in the coatings vary with process parameters from smooth surface to a nodular growth. For example, in 5 wt.% Cu deposits, the smooth features found at a small current density (j) of 2 $\text{mA}\cdot\text{cm}^{-2}$ can coarsen to faceted-dendritic features with an increase in current density to 3 $\text{mA}\cdot\text{cm}^{-2}$, and further yet to nodular features at 5 $\text{mA}\cdot\text{cm}^{-2}$.

The crystallite size of each deposit is quantified using the Debye-Scherrer formulation for peak-broadening of the Bragg reflections in the x-ray diffraction scans. The current density is seen to affect the grain size. The grain size (d_g) decreases inversely with an increase in the current density (j). Two regimes can be distinguished based on the duration of the on-time for the current pulse (t_p). A short pulse ($t_p < 5$ msec) regime shows a faster decrease in d_g with increasing j than does the long pulse ($10 < t_p < 30$ msec) regime. Also, we have found in depositing Au-Cu from cyanoalkaline-based solutions, as commonly reported, that a decrease in the current density and cell potential favor deposition of the more noble metal species.

The use of a pulsed-current is well known to refine the grain size of the electrodeposited coatings. A pulsed current facilitates nuclei formation as the peak current density can be considerably higher than the limiting direct-current density. It's observed that grain size refinement at the nanoscale is enhanced for the Au-Cu electrodeposits at greater current densities as the pulse duration (t_p) is decreased from 10-30 msec to < 5 msec. This result may suggest a difference in the energetic barrier for stabilization of grain size between each pulse-duration mode. That is, the long pulse has an additional barrier to inhibit bulk-like diffusion whereas growth for the short pulse is primarily limited to the barriers for nucleation and surface diffusion. A difference in growth may then be apparent in the energetic barrier for grain

formation. The long pulse mode should have a barrier for grain formation (Q_{lp}) that is greater than the energy for the short pulse mode (Q_{sp}). Both Q_{sp} and Q_{lp} should be less than the activation energy obtained from high-temperature, tracer-diffusion studies.

A model is developed to determine the activation energy (Q) for grain formation. The first premise is that a classic Arrhenius-type behavior for temperature-dependent diffusion in solids is assumed for the growth of electrodeposited coatings. Assuming ideal grain growth, i.e. $d_g^2 \propto t_p$, diffusion is mitigated by a negative exponential of the activation energy (Q) relative to the deposition energy (Q^*). For the electrodeposition process, Q^* is equivalently defined as the integral product of the cell potential (U) with the total charge (q_p) in the number (n) of deposited units (i.e. ions) during each current pulse. The general expression adopted is that Q^* is proportional to $N_A \cdot (q_p \cdot n^{-1}) \cdot U$ where N_A is the Avogadro number and q_p is assumed as equal to the product of the average current density (j) with the surface area (A) of the deposited unit with the duration of the pulse (t_p). For dense packing, of the deposited units, the area (A) can be equivalently approximated as the square of the grain size (d_g^2). For deposition from a high-pH alkaline solution, singly charged ions are assumed, hence the number (n) of ions is then equivalent to the grain size area ($A = d_g^2$), divided by the area of a unit cell (A_o). Noting that the unit cell area (A_o) is equivalent to the square of the average Au-Cu lattice parameter (a_o), Q^* can be expressed as equivalent to $N_A \cdot (j \cdot t_p \cdot a_o^2) \cdot U$.

In a plot of $(Q^*)^{-1}$ with $\ln[\partial(d_g^2 \cdot t_p^{-1})]$, a straight line is found, as anticipated – the slope of which is equivalent to $-Q$. An activation energy (Q) for grain formation in the long-pulse mode (Q_{lp}) is equal to 1.52 $\text{eV}\cdot\text{atom}^{-1}$ and for the short-pulse mode (Q_{sp}) it's equal to 0.16 $\text{eV}\cdot\text{atom}^{-1}$. As first seen in the grain size variation with current density, there are two regimes for nanocrystalline growth – a short and long pulse mode, each with a distinct activation energy. For comparison, an activation energy (Q_T) for grain growth of 1.85 $\text{eV}\cdot\text{atom}^{-1}$ is reported for high-temperature tracer diffusion studies of Au^{198} in both Au and Cu. As anticipated, $Q_{sp} < Q_{lp} < Q_T$.

Of interest is the transition in the growth structure that corresponds with a change in the kinetics of the deposition process. A range of diffusion is available for either the short-pulse or long-pulse mode to produce a smooth Au-Cu surface. A smooth surface results when $\ln D$, i.e. $\ln[\partial(d_g^2 \cdot t_p^{-1})]$, is greater than -22.0 for either the short- or long-pulse mode. The surface features roughen, i.e. become nodular, when the kinetics slow down to $-22 < \ln D < -26$.

In summary, empirical relationships are developed that relate the parameters of the deposition process to the morphology and grain size at the nanoscale. Regimes for nanocrystalline growth include a short and long pulse mode, each with distinct activation energies. The long pulse has the additional contribution of bulk-like diffusion whereas the short pulse is limited to surface diffusion and nucleation. For either pulse condition, a transition from a rough (or nodular) growth to a smooth surface results with an increase in the kinetics of diffusion.

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